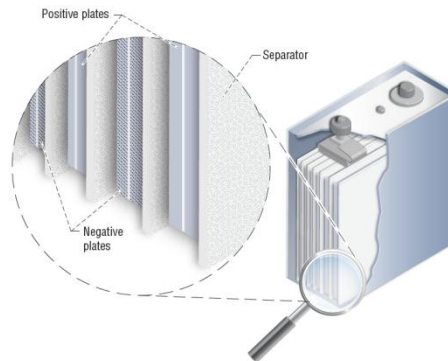
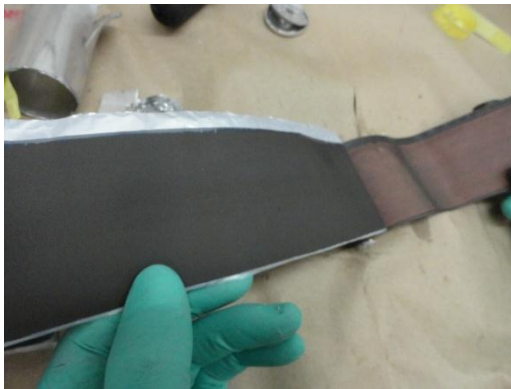




# A Summary on Progress in Materials Development for Advanced Lithium-ion Cells for NASA's Exploration Missions



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Blue Origin Power TIM

December 14, 2011



# Li-Ion Battery Development



Objectives: Develop Flight Qualified, Human-Rated Li-Ion cells with increased reliability and mass and volume reductions

Approach:

- Identify chemistries most likely to meet overall NASA goals and requirements within allotted development timeframe
  - “High Energy” and “Ultra High Energy” cells targeted to meet customer requirements
- Utilize in-house and NRA Contracts to support component development
  - Develop components to increase specific energy (anode, cathode, electrolyte)
  - Develop low-flammability electrolytes, additives that reduce flammability, battery separators and functional components to improve human-safety;
- Engage industry partner - multi year contract with Saft America
  - Provide recommendations for component development / help screen components
  - Scale-up components (core)
  - Manufacture evaluation and screening cells
  - Design and optionally manufacture flightweight cells that address NASA's goals
- Complete TRL5 and TRL6 testing at NASA
- Leverage outside efforts
  - Utilize SBIR/IPP efforts
  - Leverage work at DoE and other government agencies

Cell development TRL definitions

TRL 4: Advanced cell components integrated into a flight design cell

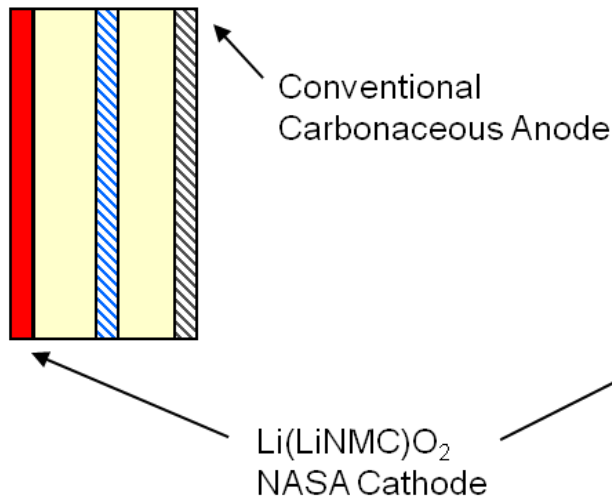
TRL 5: Performance testing on integrated cell shows goals met

TRL 6: Environmental testing on cell (vibration, thermal) shows robust performance



# Advanced Li-ion Cell Development

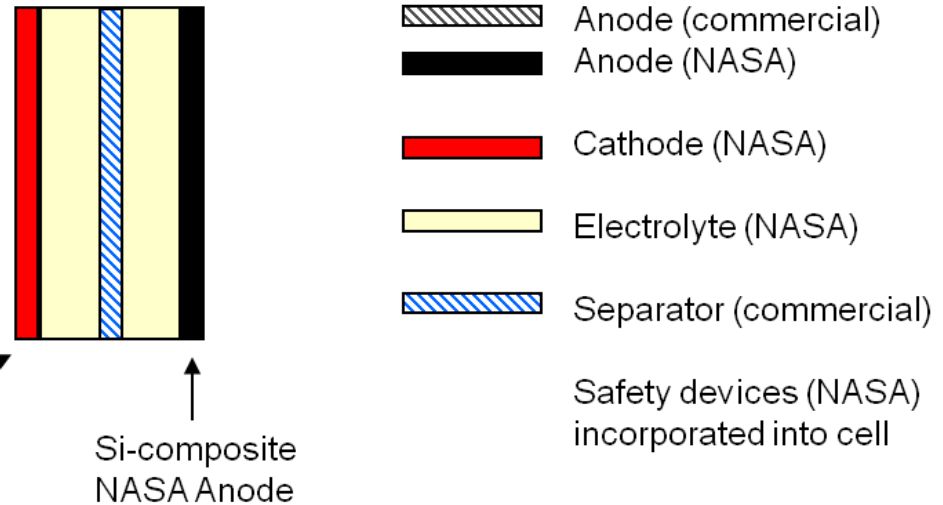
## High Energy Cell



### High Energy Cell

- Lithiated mixed metal-oxide cathode Li(LiNMC)O<sub>2</sub>/ Graphite anode
- **180 Wh/kg** (100% DOD) @ cell-level, 0° C and C/10
- 80% capacity retention at **~2000** cycles
- Tolerant to electrical and thermal abuse with no fire (overcharge, over-temperature, reversal, short circuits)

## Ultra High Energy Cell



### Ultra High Energy Cell

- Lithiated mixed metal-oxide cathode (Li(LiNMC)O<sub>2</sub>)/ Silicon composite anode
- **260 Wh/kg** (100% DOD) @ cell-level, 0° C and C/10
- 80% capacity retention at **~200** cycles
- Tolerant to electrical and thermal abuse with no fire (overcharge, over-temperature, reversal, short circuits)



# Key Performance Parameter Table

## Space Power Systems Project, Battery Key Performance Parameters

Customer Need	Performance Parameter	State-of-the-Art (EVA Portable Life Support System)	Current Value	Threshold Value	Goal
<b>Safe, reliable operation</b>	No fire or flame	Instrumentation/ controllers used to prevent unsafe conditions. Not tolerant to internal short circuit. Flammable electrolyte.	Improved component level safety over SOA (flame-retardant electrolyte, exotherm-suppressing cathode coating)	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and short circuits with no fire or thermal runaway**	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and short circuits with no fire or thermal runaway***
<b>Specific energy</b>	<b>Battery-level</b> specific energy* [Wh/kg]	113 Wh/kg at C/10 & 20°C	174 Wh/kg at C/10 & 10°C to 2.0 V/cell, (Projected)	168 Wh/kg at C/10 & 10°C	225 Wh/kg at C/10 & 10°C
<b>EVA:</b> 325-420 Wh/kg  100 cycles (with and without 30% margin)	<b>Cell-level</b> specific energy* [Wh/kg]	190 Wh/kg at C/10 & 20°C, 500 cycles at 20°C Charge/Discharge	218 Wh/kg at C/10 & 10°C to 2.0 V (Projected – using demonstrated performance extrapolated to KPP conditions)	211 Wh/kg at C/10 & 10°C to 2.0 V; 200 cycles	265 Wh/kg at C/10 & 10°C to 2.0 V; 200 cycles
	<b>Cathode-level</b> specific capacity [mAh/g]	170 mAh/g at C/10 & 20°C (Lithium-Cobalt Oxide )	252 mAh/g at C/10 & 20°C to 2.0 V (Measured)  231 mAh/g at C/10 & 10°C and 2.5 V (Projected)	270 mAh/g at C/10, 10°C & 2.5 V, 1.5 g/cc; 250 cycles	295 mAh/g at C/10 & 10°C to 2.5 V, 1.5 g/cc; 250 cycles
	<b>Anode-level</b> specific capacity [mAh/g]	328 mAh/g at C/10 & 20°C (Carbon)	1250 mAh/g at C/10 & 20°C to 1.0 V (Measured)  1250 mAh/g at C/10 & 10°C (Projected)  1130 mAh/g at C/10 & 20°C after 250 cycles (Measured)	1000 mAh/g at C/10 & 10°C to 1.0 V, and 3.7 mAh/cm <sup>2</sup> ; 250 cycles	1200 mAh/g at C/10 & 10°C to 1.0 V, 3.7 mAh/cm <sup>2</sup> ; 250 cycles
	<b>Battery-level</b> energy density [Wh/l]	199 Wh/l	440 Wh/l	430 Wh/l	520 Wh/l
	<b>Cell-level</b> energy density [Wh/l]	520 Wh/l	573 Wh/l	560 Wh/l	675 wh/l
<b>Operating environment</b>	Operating Temperature	-20°C to +60°C	10°C to +30°C	10°C to +30°C	10°C to +30°C

9-Dec-11

\*Battery and cell values are assumed at 100% DOD and discharged to 2.0 volts/cell. Assumes 18650 cells for Threshold Values and lightweight cell and battery packaging for Goal Value. Unoptimized battery packaging for SOA.

\*\*Over-temperature up to 110°C; reversal with 150% excess discharge @ 1C; pass external short tests; overcharge fully charged cell @ C/5 for 5 hours.

\*\*\*Over-temperature up to 110°C; reversal with 150% excess discharge @ 1C; pass external and simulated internal short tests; overcharge fully charged cell at 1C for 6 hours with 12 Volt limit



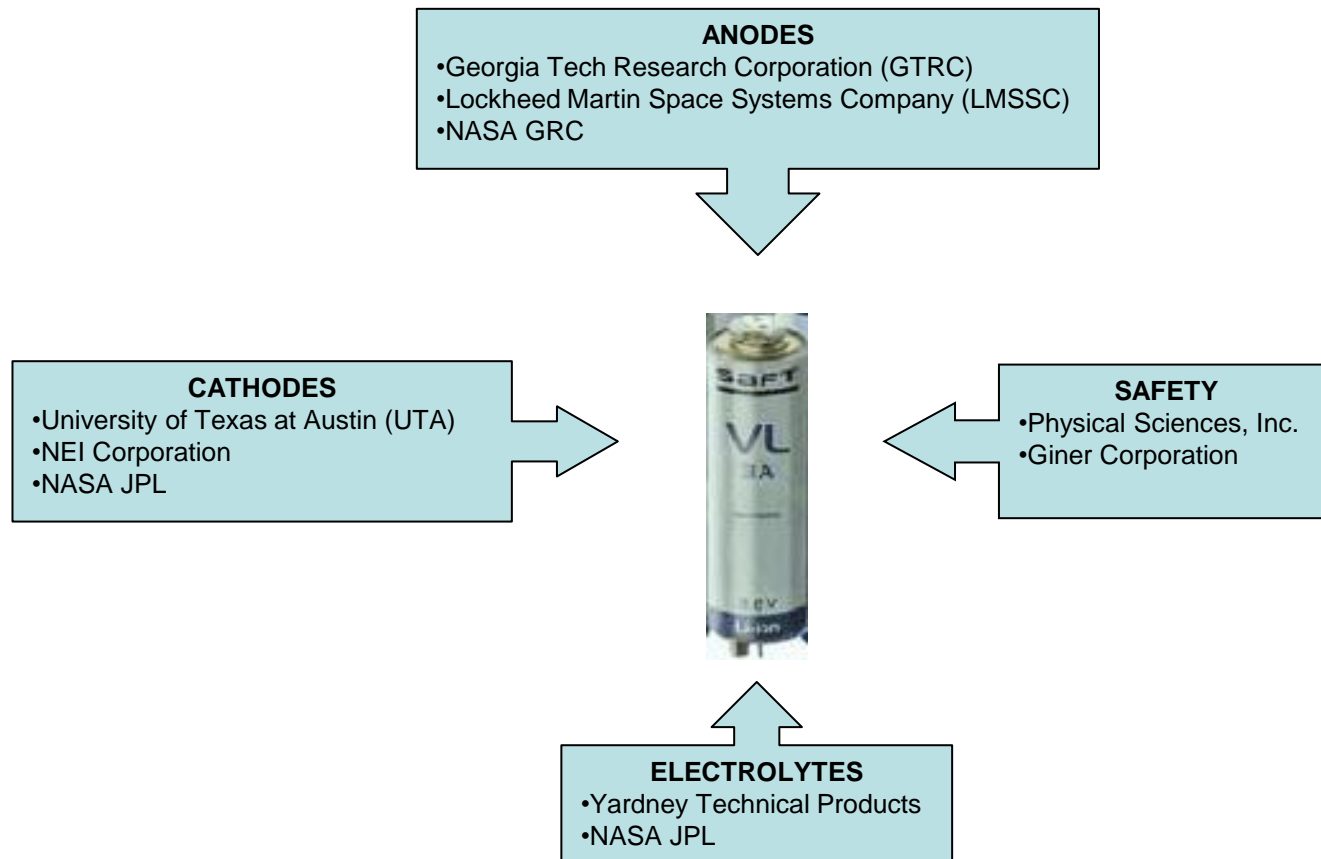
# Energy Storage Project Lithium-Ion Cell Development

Two parallel cell development approaches to meet customer requirements:

- High Energy Cell Development
  - Safe, reliable Li-ion cell with improved specific energy and energy density over SOA and good cycle life
  - Combination of newly developed cathode, electrolyte, and separator with a carbonaceous anode with known heritage and performance
- Ultra High Energy Cell Development
  - Safe, reliable Li-ion system with greatly improved specific energy and energy density over SOA and low cycle life
  - Very high energy system for applications where mass and volume reduction is enabling and cycle requirements are benign
  - Combination of newly developed anode cathode, electrolyte, and separator
  - Higher developmental risk than High Energy Cell
    - Much higher gains in component level specific capacity over conventional electrode materials required for success
    - Addition of a developmental anode increases risk in areas of electrochemical performance, sufficient maturity by need dates, and scalability and manufacturability.
    - Lithium-alloy anode and higher energy chemistry are inherently less safe – component-level inherent safety features more critical



# Development Goals Were Addressed Through a Combination of Contracted Efforts (NRA, SBIR) and NASA In-house Efforts





# NASA Exploration Technology Development Program Energy Storage Project



## **NASA In-House Efforts**

- Layered Metal Oxide Cathode Development – JPL
- High Voltage, Flame Retardant Electrolyte Development – JPL
- Si-based Composite Anode Development – GRC
- Safety Assessments – JSC
- Separator Assessments - GRC

## **NASA Research Announcement NNC08ZP022N Research and Development of Battery Cell Components**

- NEI Corp., “Mixed Metal Composite Oxides for High Energy Li-ion Batteries”
- University of Texas at Austin, “Development of High Capacity Layered Oxide Cathodes”
- Lockheed Martin Space Systems Company, “Advanced Nanostructured Silicon Composite Anode Program”
- Georgia Tech Research Corp. & Clemson University, “Design of Resilient Silicon Anodes”
- Yardney, “Flame-retardant, Electrochemically Stable Electrolyte for Lithium-ion Batteries”
- Physical Sciences, “Metal Phosphate Coating for Improved Cathode Material Safety”
- Giner, “Control of Internal and External Short Circuits in Lithium-Ion Batteries”

## **Component Scale-up and Cell Design and Development for High Energy and Ultra High Energy Cells**

- Saft America



# Summary of Two Years of NRA Contract Cathode Development

## On Target:

- In Year One, very low first cycle reversible capacity was measured on all cathode deliverables (50-70% of charge capacity was delivered on the first discharge).
  - ✓ First cycle reversible capacity has improved and on some materials is now better than that of typical Li-ion cathodes.
- First year manufacturability studies revealed that Tap Density, a critical metric for raw powders, was too low to fabricate practical cathodes. Development efforts were directed to improve tap density in their second year.
  - ✓ Tap Density has improved to better than the minimum value necessary by using alternate synthesis methods (1.5 g/cc minimum).
- Specific capacity declined as a result of change in cathode synthesis methods to improve tap density.
  - ✓ Optimizations were performed to maximize specific energy while maintaining tap density at or above minimum levels necessary for manufacturability.

## Still need improvement (current values not yet at or approaching goals):

- Specific Capacity, both at room temperature and at lower temperatures
- Temperature performance (percentage of room temperature capacity retained at 0° C)
- Discharge rate capability
- Cycle life
- **Combination of attributes that meet or exceed goals in one material**





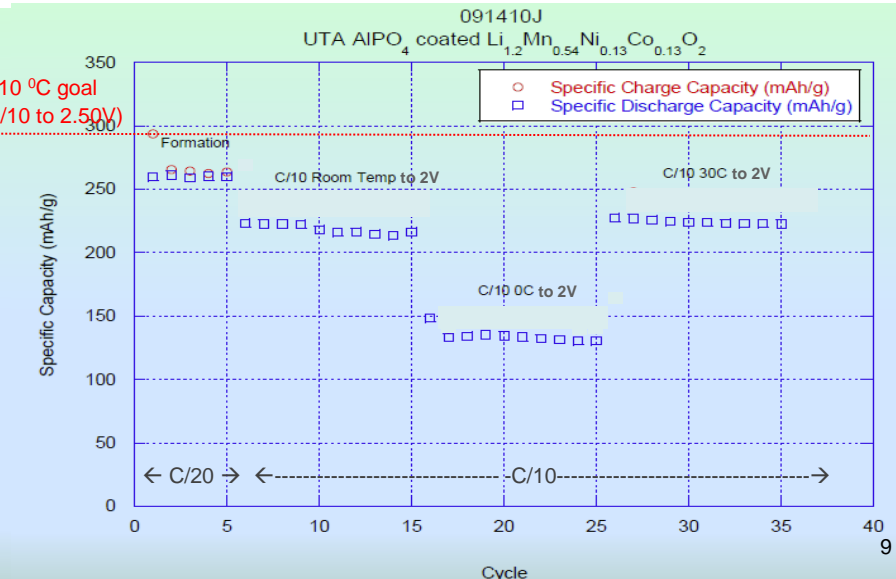
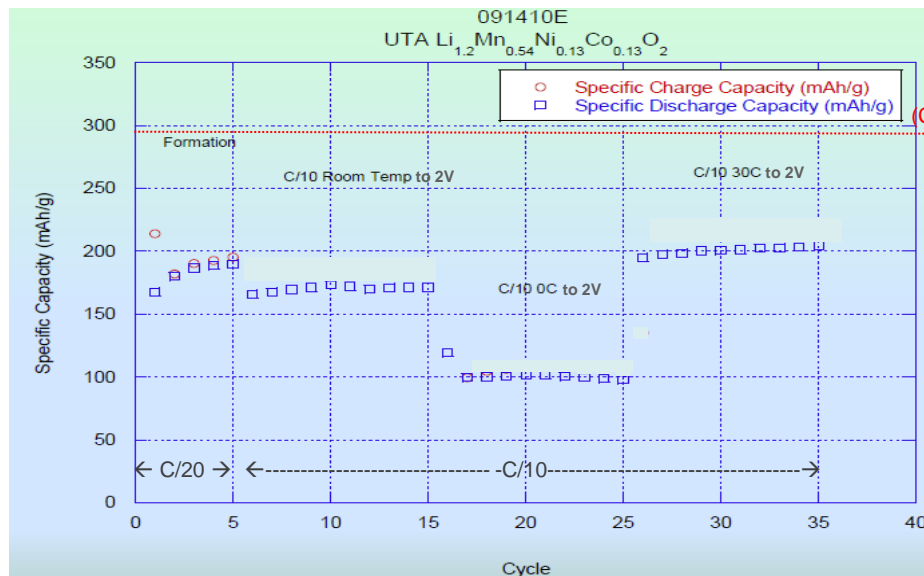
# Performance of University of Texas at Austin (UTA) NMC Cathodes

## Accomplishments:

- Improvements in specific capacity, 1<sup>st</sup> cycle reversible capacity and temperature performance
- Tap density exceeds goals required for manufacturability
- Successful use of alternative cathode synthesis procedures and application of coatings to improve tap density and material performance
- Coated materials exhibit improved performance over uncoated
- Several conference papers and publications

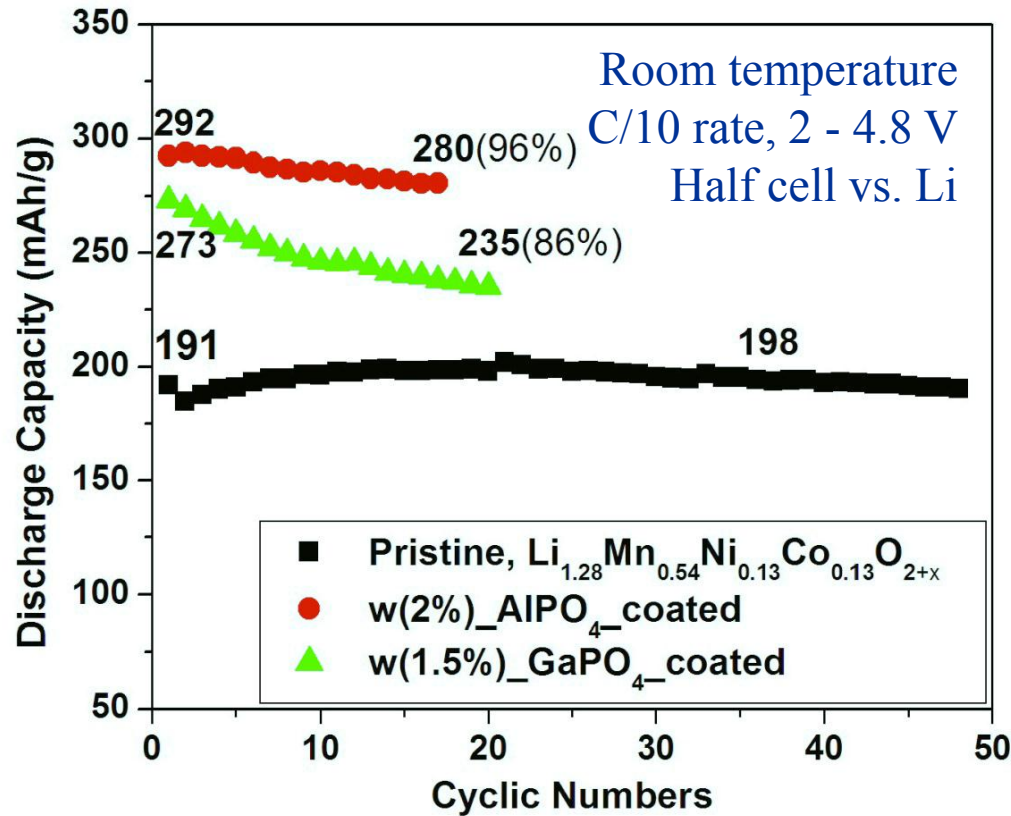
## Remaining Challenges to meet goals:

- Higher specific capacity at RT and low temperatures
- Better temperature performance (higher percentage of RT capacity retained at low temperatures)
- Improved rate capability
- Demonstrated cycle life
- Combination of attributes that meet or exceed goals in one material





# University of Texas at Austin Cathode Development Follow-on Effort Preliminary Results



*Surface modification of the optimized sample demonstrates an initial specific capacity of 292 mAh/g and high tap density ( $>1.8 \text{ g/cm}^3$ ).*



# Summary of Two Years of NRA Contract Si-composite Anode Development

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## On Target:

- Specific capacity at C/10 and 0° C has exceeded goal value, outperforming SOA carbonaceous anodes by >3X (>1200 mAh/g vs. ~372 mAh/g).
- Excellent capacity retention has been achieved at 0° C, and has a tendency to improve with cycling in some materials.
- Rate capability at C/2 has exceeded that of SOA carbonaceous anodes (as % of C/10 capacity retained at C/2 rate and RT).
  - 93% for MPG-111 and >94-100% in Si:C anodes.

## Still need improvement (current values not yet at or approaching goals/metrics of SOA materials):

- Reversible capacity
- Loading
- Coulombic efficiency
- Demonstration of cycle life in cells

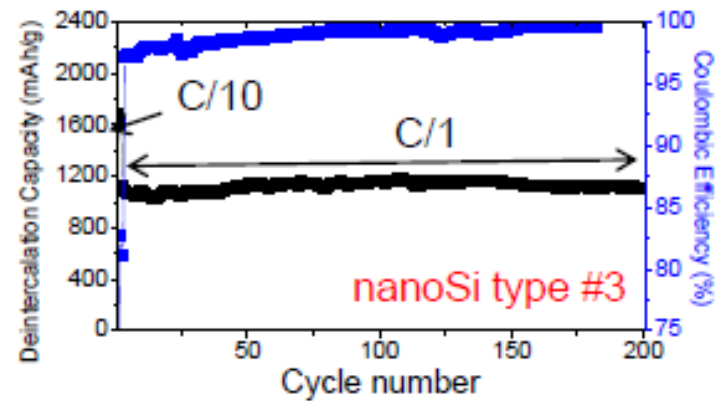
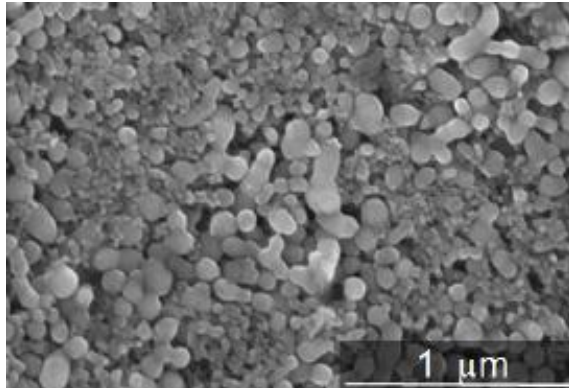


# Ultra High Energy Lithium-ion Battery Anode Development

Georgia Institute of Technology (GT) and Georgia Tech Research Corporation (GTRC)  
in partnership with Clemson University

## Anode Material:

Nano-silicon-carbon composite with binder



Achieved >1100 mAh/g capacity at a C/1 rate for 200 cycles with GT materials. Data was collected at GT.

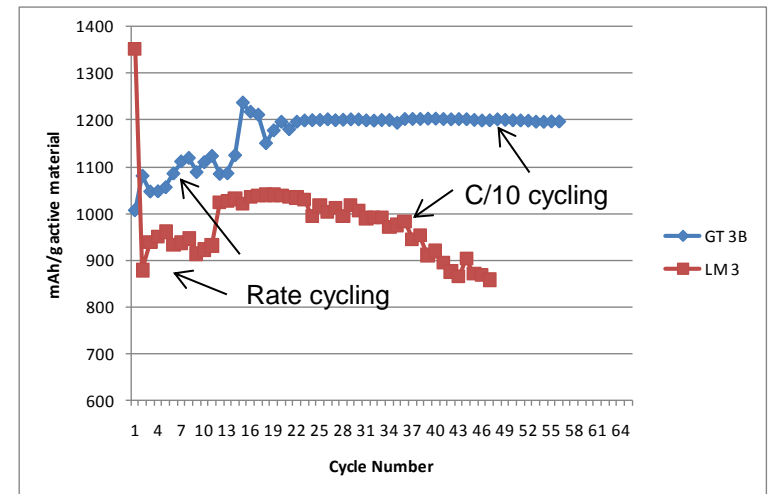
## Fundamental Studies Addressed:

- Binder properties & modifications
- Electrolyte additives
- Silicon-binder interfacial properties
- Silicon SEI properties
- Cell “conditioning” effects
- Theoretical modeling

## Technical Issues:

- SEI stabilization to reduce capacity fade
  - Optimal cell “conditioning” parameters
- Low electrode loading
- Stabilization of silicon volume changes
- Optimal electrolyte composition, salts & additives to achieve long-term cycling ability

Technical approaches to address these issues have been proposed

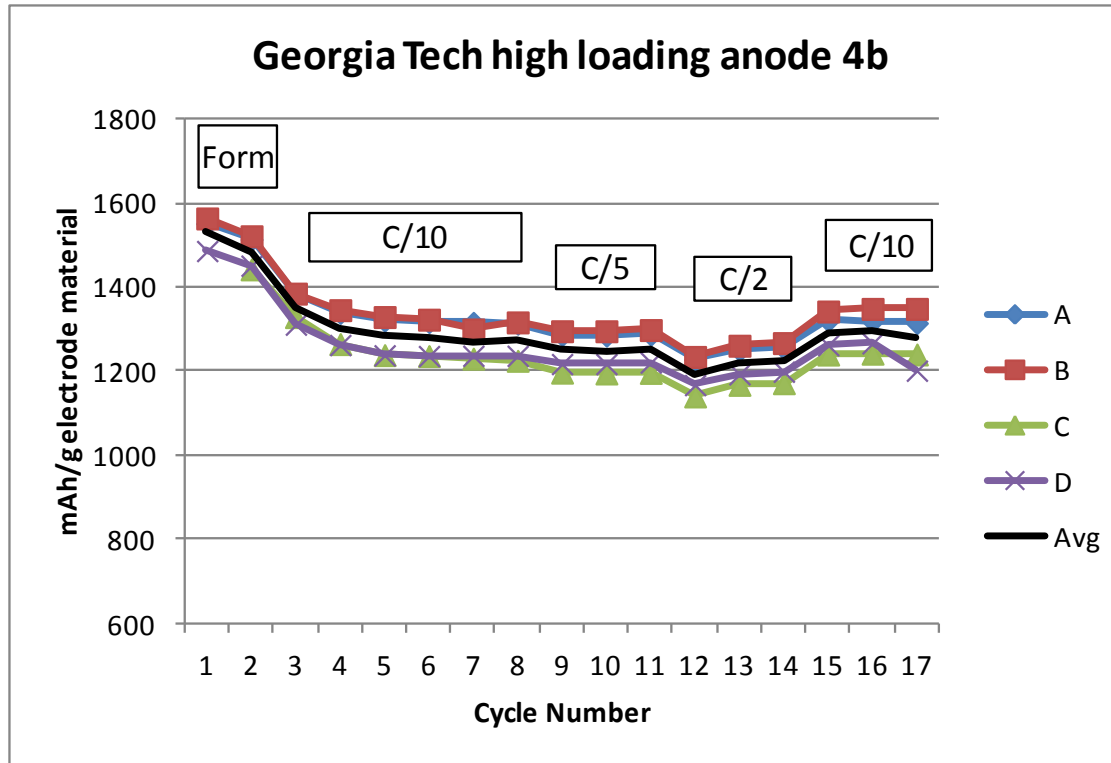


Half-cell cycling performance of a GT anode (blue) compared to Lockheed Martin Space Systems Company (LMSSC) anode material (red) [stable capacity retention on GT materials achieved with the addition of VC (vinylene carbonate) to the electrolyte, no impact on LMSSC materials]



# Georgia Tech Anode Development Follow-on Effort

## Preliminary Results



Total electrode material mass loading of 2.2 – 2.6 mg/cm<sup>2</sup> (based upon loading needed to match NMC cathode in a full cell)

- High-loading anodes demonstrated better specific capacity than the low-loading anodes during the initial cycles (>1300 mAh/g at C/10 at both 20° C & 0° C), but demonstrated significant capacity fade with continued cycling
- High-loading anodes cycled at C/2 & 20° C at GRC showed capacity fade to ~600 mAh/g after ~75 cycles, whereas the low-loading anodes demonstrated superior cycle-life performance with continued high capacity ( > 80% retention at >250 cycles & 23° C)



# Electrolytes

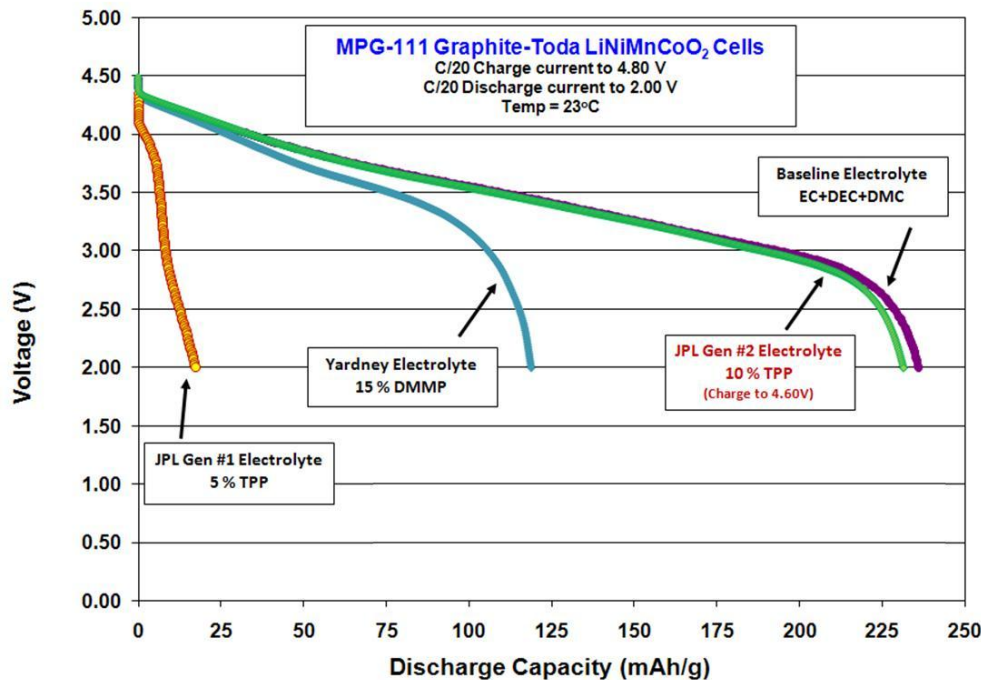
- Goal: Develop flame-retardant and/or non-flammable electrolytes that are stable up to 5V

Technology Challenges	Current approaches to address
Electrolyte that is stable up to 5V.	Experiment with different electrolyte formulations and additives with potential to improve high voltage stability. Study interactions at both electrodes.
Non-flammable or flame retardant electrolyte.	Develop electrolytes containing additives with known flame retardant properties. Perform flame retardance assessments on developments that exhibit suitable electrochemical performance.
High voltage stable, non-flammable or flame retardant electrolyte (combination of both properties in one electrolyte system).	Combine flame retardant additives with electrolyte formulations with high voltage stability. Operate systems to high voltages and investigate impacts on rate capability, specific energy, energy density and life.
Electrolytes possessing the requisite physical properties to ensure good rate capacity (adequate conductivity) and compatibility (wettability).	Develop electrolytes that are not excessively viscous to ensure that the ionic conductivity is sufficiently high over the desired temperature range and the separator wettability is adequate.



# Electrolytes

➤ Flame-retardant electrolytes containing triphenyl phosphate (TPP) display good self extinguishing properties and stability at high voltages (4.8V), and exhibit excellent capacity retention and cycling stability in cells containing graphite



Discharge capacity of graphite-Li(LiNiMnCo)O<sub>2</sub> cells at high voltage with NASA JPL TPP-containing electrolytes as compared to an all carbonate-based formulation

Description	Electrolyte	Percentage Flame Retardant Additive	SET/s	Standard Deviation
"Baseline" Electrolyte	1.0M LiPF <sub>6</sub> in EC/EMC (3:7)	None	33.4	3.4
JPL GEN #1 Electrolyte	1.0M LiPF <sub>6</sub> in EC/EMC/TPP (2:7.5:0.5) + 2% VC	5% TPP	22.45	2.3
JPL Electrolyte	1.0M LiPF <sub>6</sub> in EC/EMC/TPP (2:7:1) + 2% VC	10% TPP	9.57	0.9
JPL Electrolyte	Salt and carbonate blend	15%TPP	3.78	1.2
Yardney/URI GEN #2 Electrolyte	1.0M (95% LiPF <sub>6</sub> + 5% LiBOB) in EC/EMC/DMMP (3/5.5/1.5)	15% DMMP	1.8	1.5
Yardney/URI GEN #1 Electrolyte	1.0M (95% LiPF <sub>6</sub> + 5% LiBOB) in EC/EMC/DMMP (3/5/2)	20% DMMP	0.4	0.4

Self-Extinguishing Times of Developmental Electrolytes.  
 Data was generated by the University of Rhode Island.

Next steps:

- Optimization of flame-retardant electrolytes that are compatible with Si
- Incorporate electrolyte advancements into production cells





# Summary of Safety Component Development with Physical Sciences, Inc. (PSI)

## Objective:

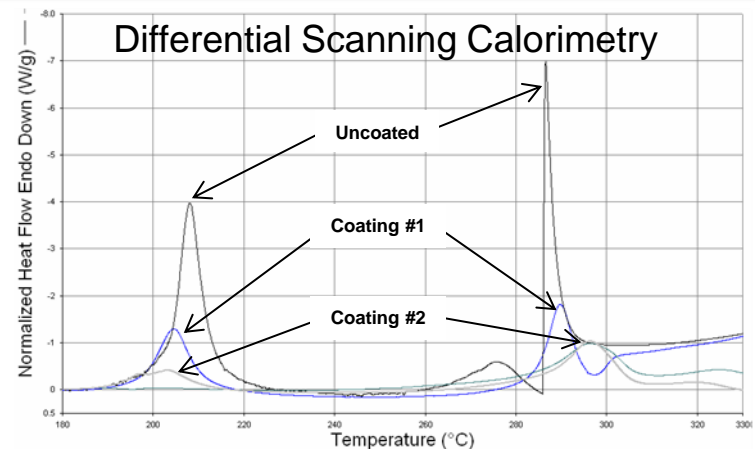
- Coat metal oxide cathode powders with lithium cobalt phosphate coatings to improve thermal stability.

## Accomplishments:

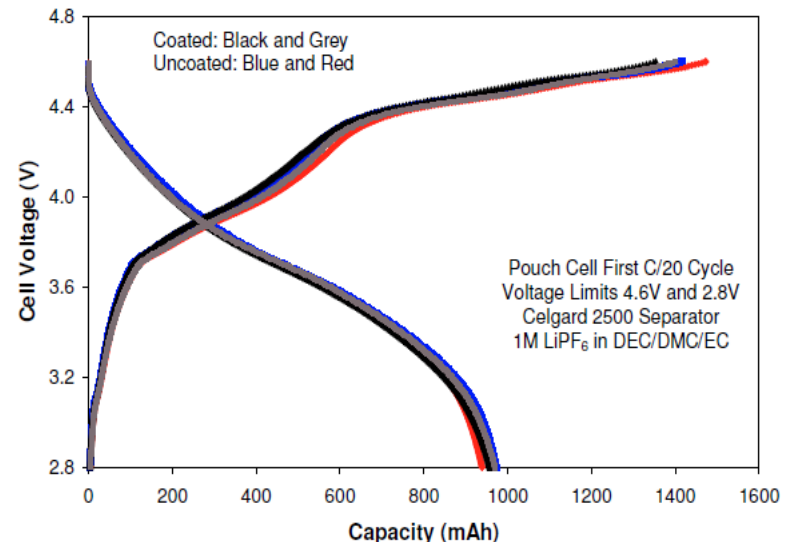
- Demonstrated robust adhesion of coating on  $\text{LiCoO}_2$  cathodes in half cells for 200 cycles, cycling at C-rate with capacity retention of ~90% of 1st cycle capacity.
- Developed coating and processes to coat NMC cathode materials.
- Coated TODA 9100 NMC cathodes demonstrated <1% loss in discharge capacity over 50 cycles at a C/5 rate.
- Demonstrated to reduce exotherms without reducing performance on high voltage cathodes (Toda 9100 NMC).
- Higher capacity, higher tap density lower irreversible capacity, and better cycling stability demonstrated on coated Toda 9100 NMC cathodes as compared to uncoated cathodes.

## Next steps:

- Physical Sciences, Inc.
  - Coat NEI 23 mo. deliverable with coating and process developed for Toda NMC materials.
- Under separate effort (most likely with Saft)
  - Produce electrodes from PSI-coated NEI cathodes.
  - Build cells containing PSI-coated NEI cathodes.
- NASA independent assessments:
  - Determine impact on safety and abuse in full cells.
  - Demonstrate cycling, rate, and low temperature performance.



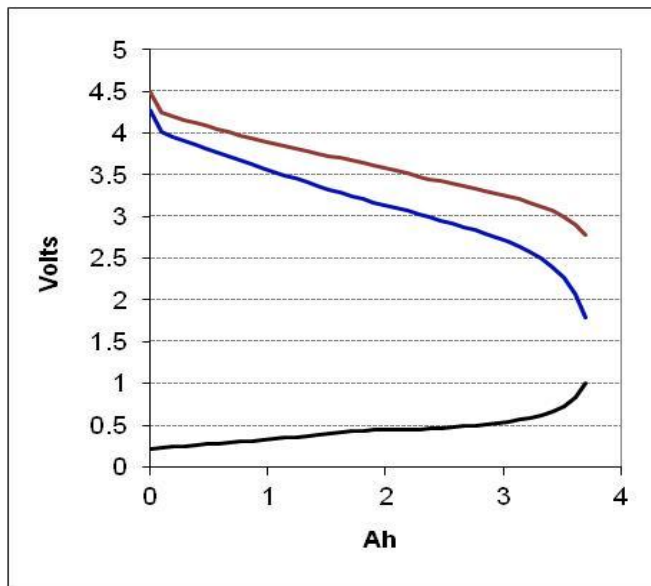
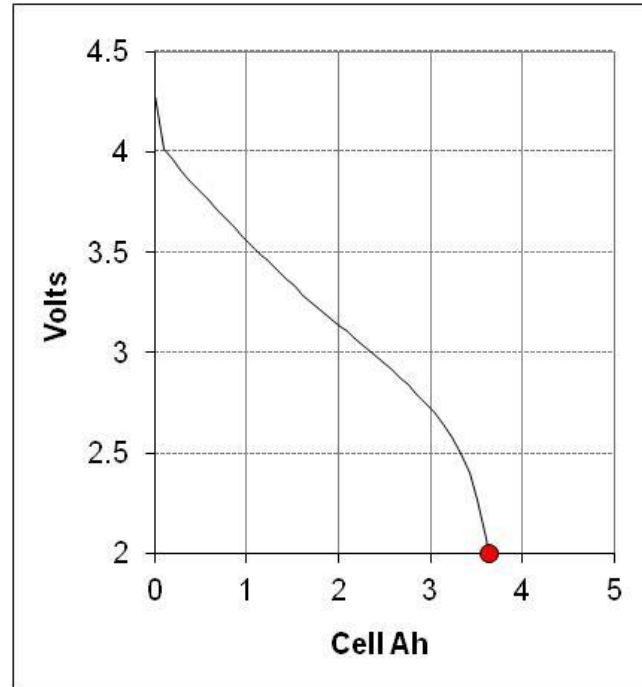
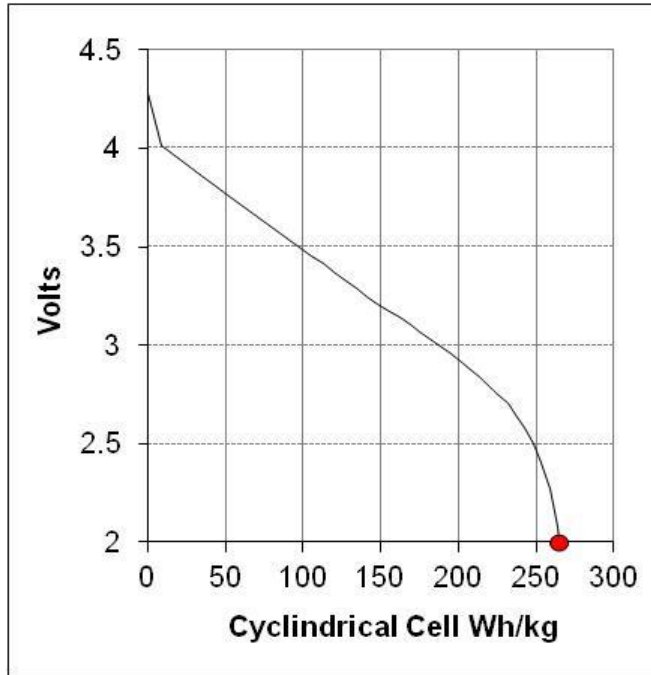
Preliminary results show reduced heat flow in exotherms of coated Toda 9100 NMC cathode. Data was collected at PSI.



Cells containing uncoated and coated TODA 9100 NMC (2 cells of each) display similar first cycle capacity. Data was collected at PSI.



# 18650 Cell Full Performance Prediction at 10°C

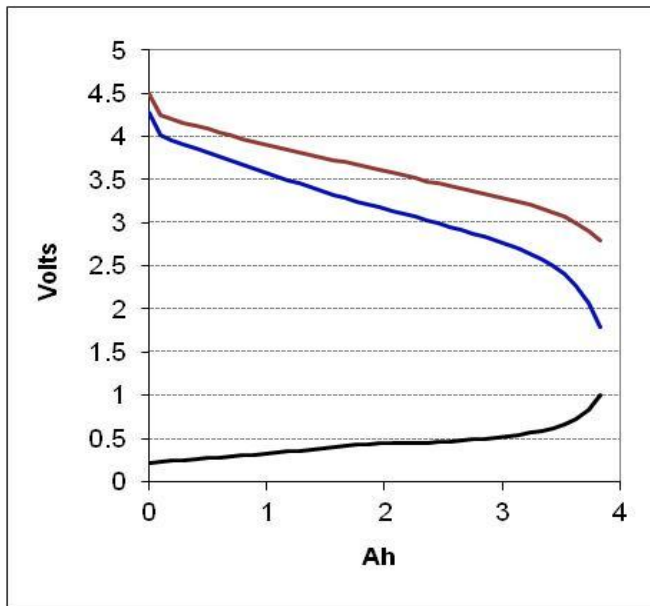
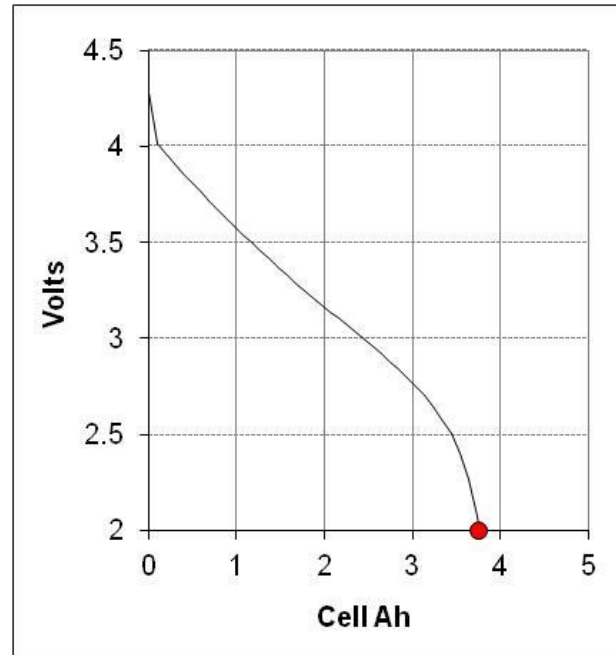
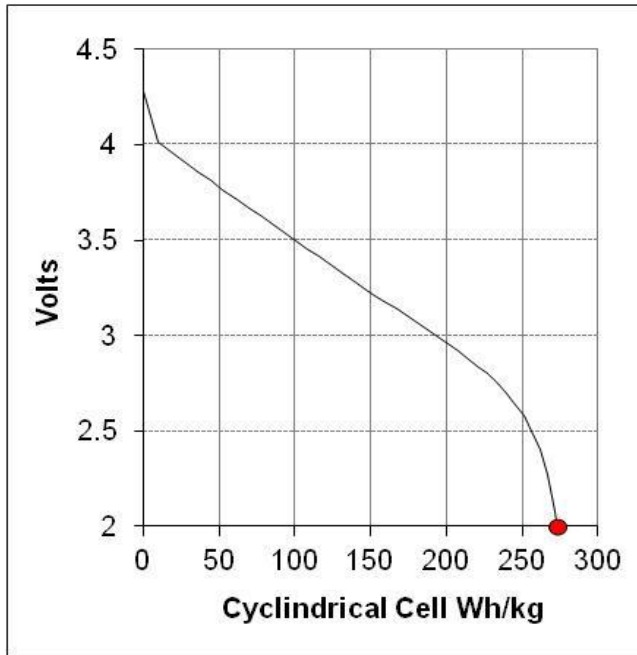


Wh/Kg	265
Wh/l	708
Ah	3.64
Cell weight (g)	44.1

Performance projected based on assumption that individual components meet goal values for battery KPP's dated 9/22/2011

Goals: 10oC		Cell Voltage (V)
Ah	Wh/kg	
0.00	0.00	4.28
0.10	8.95	4.02
0.19	17.55	3.96
0.29	26.04	3.91
0.38	34.42	3.86
0.48	42.69	3.81
0.57	50.86	3.77
0.67	58.93	3.72
0.76	66.90	3.67
0.86	74.77	3.63
0.95	82.54	3.58
1.05	90.22	3.54
1.14	97.81	3.50
1.24	105.31	3.45
1.33	112.71	3.41
1.43	120.02	3.37
1.52	127.24	3.33
1.62	134.37	3.29
1.71	141.41	3.25
1.81	148.38	3.21
1.90	155.26	3.17
2.00	162.07	3.14
2.09	168.80	3.10
2.19	175.45	3.07
2.28	182.03	3.03
2.38	188.53	3.00
2.47	194.95	2.96
2.57	201.28	2.92
2.66	207.53	2.88
2.76	213.70	2.84
2.85	219.77	2.80
2.95	225.76	2.75
3.04	231.64	2.71
3.14	237.42	2.65
3.23	243.06	2.58
3.33	248.53	2.50
3.42	253.82	2.40
3.52	258.85	2.27
3.61	263.53	2.08
3.71	267.70	1.79
3.80	271.16	1.42
3.90	273.75	0.98
3.99	275.26	0.42
4.09	275.51	-0.19
4.18	274.43	-0.81

# 18650 Cell Full Performance Prediction at 20°C



Wh/Kg	273
Wh/l	732
Ah	3.76
Cell weight (g)	44.1

Performance projected based on assumption that individual components meet goal values for battery KPP's dated 9/22/2011

Ah	Wh/kg	Cell Voltage
0.00	0.00	4.28
0.10	9.24	4.02
0.20	18.12	3.96
0.29	26.89	3.91
0.39	35.54	3.86
0.49	44.08	3.81
0.59	52.52	3.77
0.69	60.85	3.72
0.79	69.07	3.67
0.88	77.20	3.63
0.98	85.22	3.58
1.08	93.15	3.54
1.18	100.99	3.50
1.28	108.73	3.46
1.37	116.37	3.41
1.47	123.92	3.37
1.57	131.37	3.33
1.67	138.74	3.29
1.77	146.01	3.25
1.87	153.20	3.21
1.96	160.30	3.17
2.06	167.33	3.14
2.16	174.28	3.11
2.26	181.15	3.07
2.36	187.94	3.03
2.45	194.65	3.00
2.55	201.28	2.96
2.65	207.82	2.92
2.75	214.27	2.88
2.85	220.64	2.84
2.95	226.92	2.80
3.04	233.10	2.75
3.14	239.17	2.71
3.24	245.13	2.65
3.34	250.96	2.58
3.44	256.61	2.50
3.53	262.07	2.40
3.63	267.27	2.27
3.73	272.10	2.08
3.83	276.40	1.79
3.93	279.98	1.42
4.02	282.66	0.98
4.12	284.22	0.42
4.22	284.48	-0.19
4.32	283.38	-0.80



# **NASA In-house Component Development and Fundamental Efforts**

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**In-house NASA efforts continue to address select components and technical issues necessary to continue to advance technology**

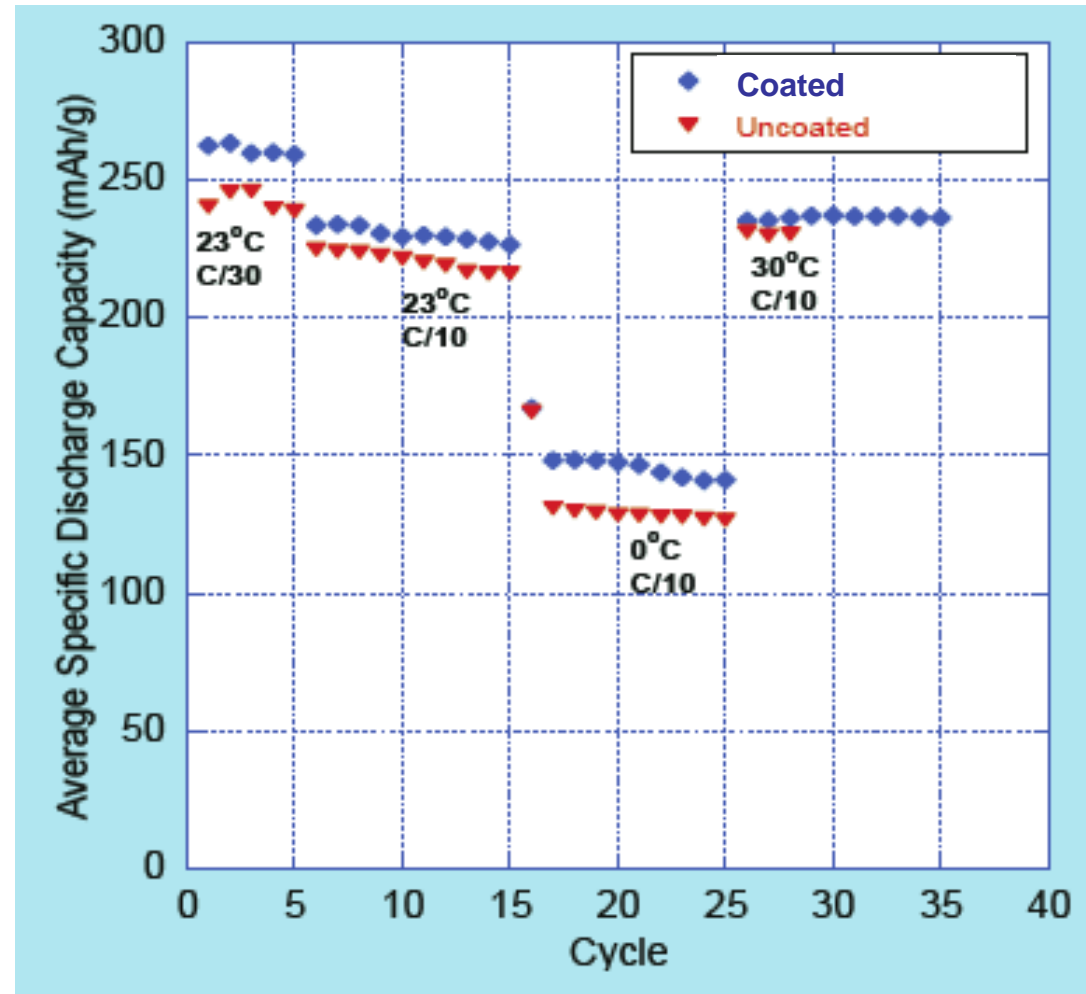
- **Anode fundamental studies**
- **Cathode development**
- **Electrolyte Development**
- **Cell Integration**



# NASA In-house Cathode Development (JPL)

## Employing mechanical methods to improve performance

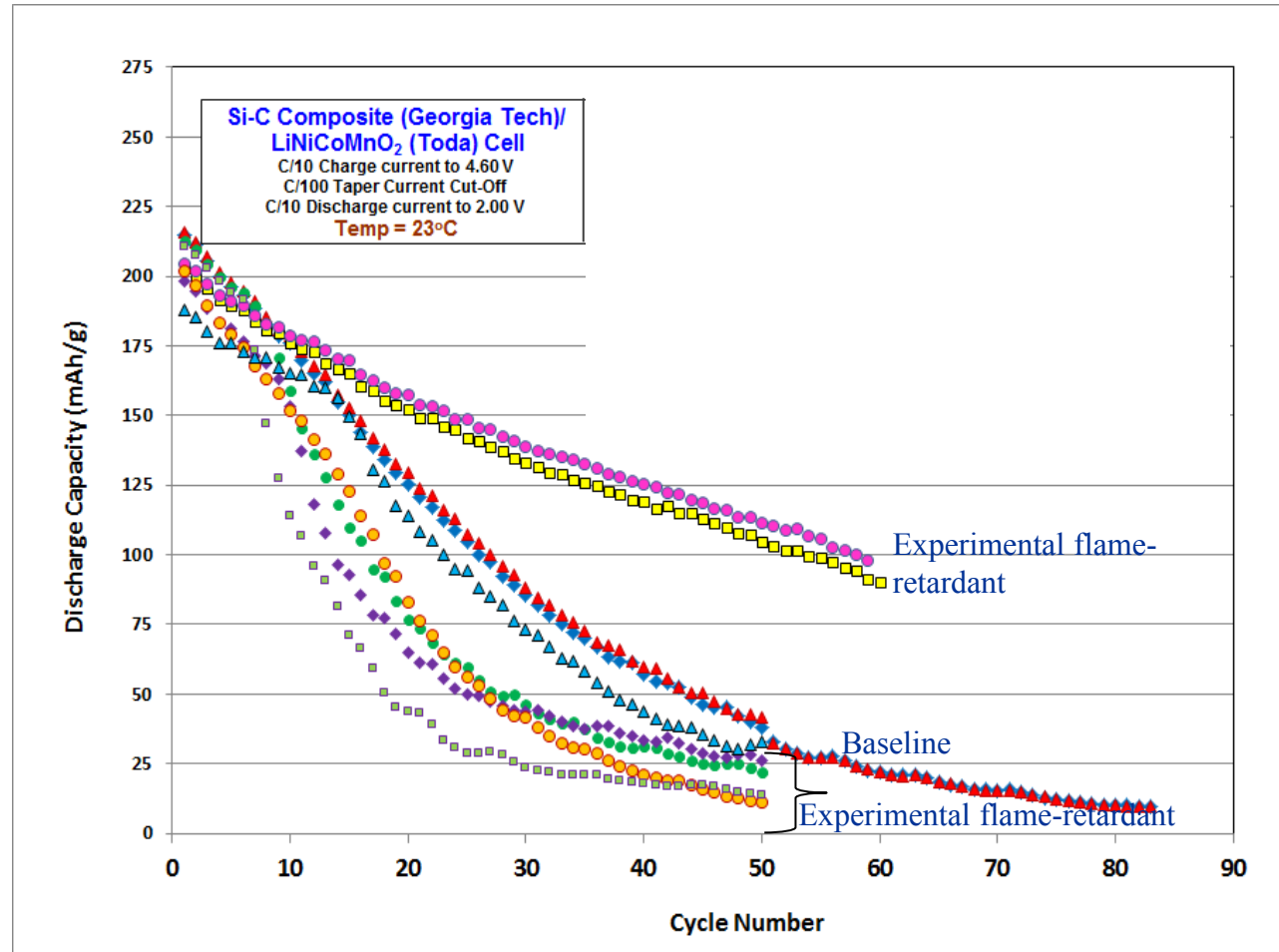
- Ball milling and annealing improved tap density ( $2.0 \text{ g/cm}^3$ )
- Surface modification improved specific capacity over uncoated samples
- Coated samples demonstrated less 1<sup>st</sup> cycle irreversible capacity loss than similar NMC materials (24 mAh/g)





# NASA In-house Electrolyte Development (JPL)

- Developing high voltage flame retardant electrolytes that are compatible with graphite/NMC and Si-based/NMC systems.
- Preliminary results show improved performance with some flame-retardant blends over baseline, however capacity fade is much greater in Si-based/NMC cells (cathode-limited) than in Si-based/Li half cells.



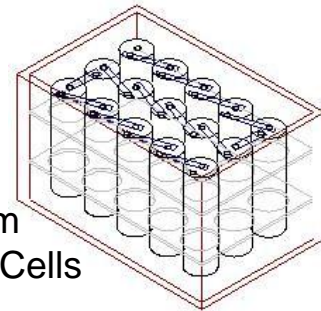


# Batteries: General Approach

- We Are Developing:
  - Si composite anodes
  - Lithiated metal oxides of Nickel, Manganese and Cobalt (NMC) cathodes
  - High voltage/low flammability electrolytes
- Our Goals Are:
  - Increase the specific energy, energy density and safety of batteries
  - Representative Mission Requirements for the Advanced EVA suit
- Research Methodology
  - Develop components
    - National experts develop specialty components
  - Assess components
    - Build /test electrodes and screening cells
    - Provide manufacturing perspective from the start
  - Scale-up components for Mfg.
  - Build and Test Cells (6.5 Ah & 10 Ah):
    - Use developed components
    - Determine baseline performance
    - Determine component interactions
    - Determine cell-level performance and safety



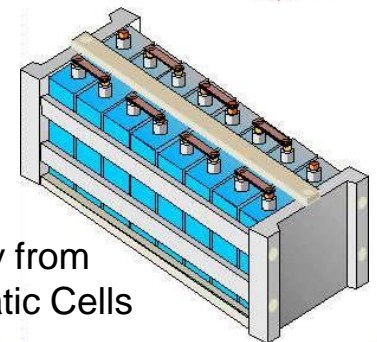
DD Cells



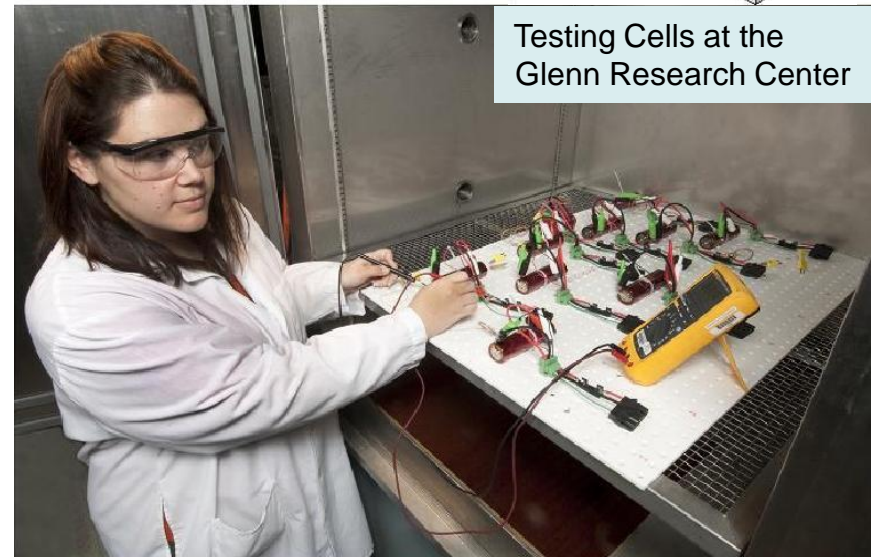
Battery from Cylindrical Cells



VL3A Cells



Battery from Prismatic Cells



Testing Cells at the Glenn Research Center





## Next steps in Developing NASA's Advanced UHE Li-ion Cells

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- Component development efforts will culminate in the delivery of components for test, verification, and integration studies at NASA and Saft America
- VL3A-design cells (nominal 6.5 Ah with standard components) are scheduled to be built with components that have reached maturity
  - Cells containing JPL flame-retardant electrolyte, commercial NMC cathode and graphite anode currently in production at Saft America
- Next sets of cells scheduled to be built March 2012
  - Will contain Georgia Tech Si-based anode, UTA NMC cathode, and JPL flame-retardant electrolyte
- Cells will be tested at NASA for electrical performance, safety and abuse



# Battery Chemistry Determination

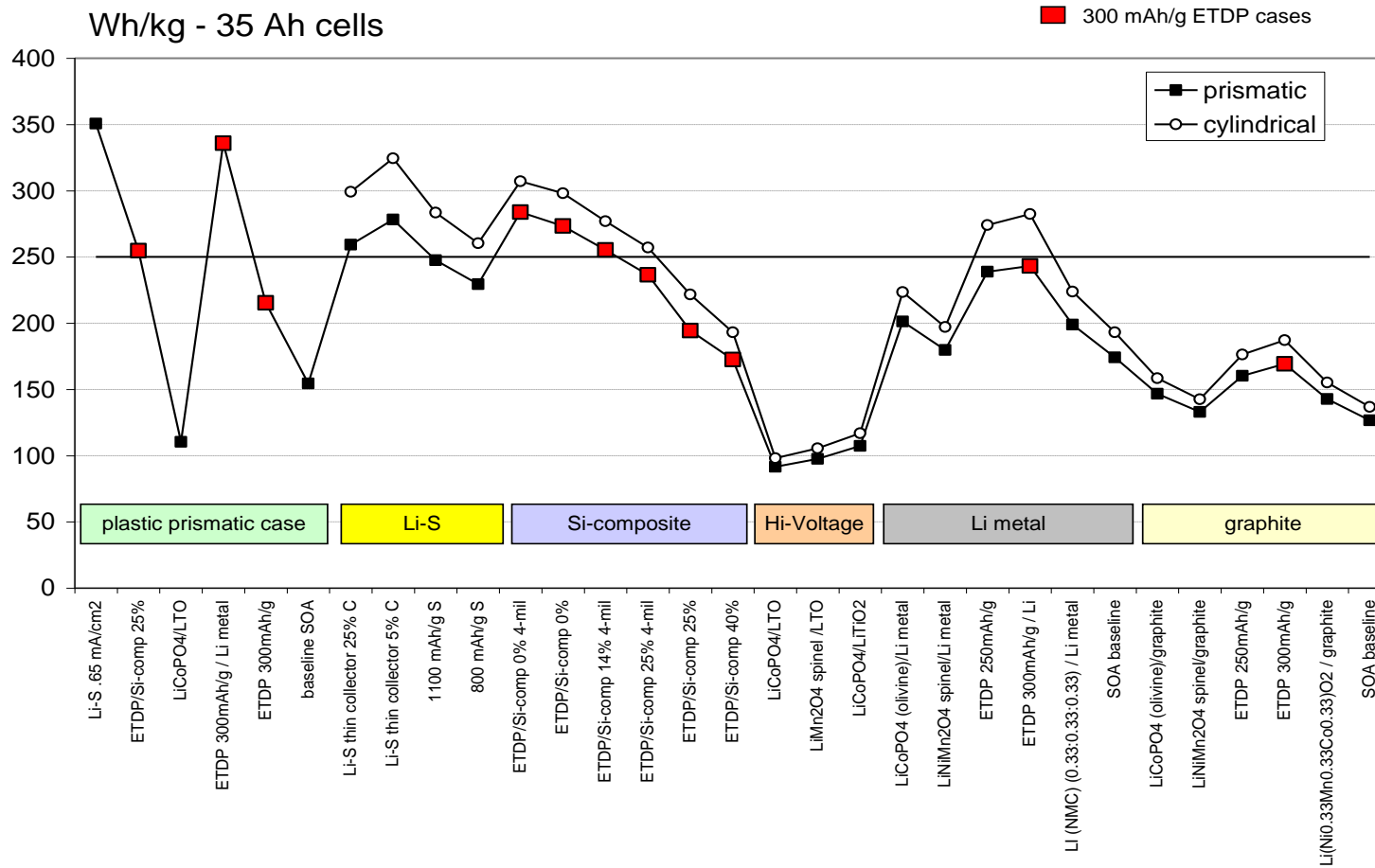
## Study Goal:

Determine the best advanced chemistry to develop for safe, reliable energy storage systems with extremely high specific energy as compared to today's state-of-the-art (SOA) batteries.

Safety target: No fire or thermal runaway at the component level.

Specific energy target: 160-220 watt-hours per kilogram delivered at the battery level at C/10 and 0°C.

Process: Assessed 31 chemistries, selected 7 as feasible, ranked those 7 using an Analytical Hierarchical Process (pairwise comparison against 10 weighted attributes)







# Future Chemistry Assessments

## Al-air

Overview:

Alkaline electrolyte versions can exceed 500 Wh/kg battery level

Model in literature forecasts 729 Wh/kg for a 204 kWh EV battery

They are complex systems, not rechargeable electrochemically (mechanical re-fueling has been demonstrated)

Aluminum corrosion issues limit wet life

Component	Sp. Energy, Wh/kg		Cell Voltage Range	TRL/Stage of Development	Advantages	Technology Challenges/Issues
	Theoretical	Experimental				
Li-S	2600	350 demonstrated; 500 -600 achievable	2.5-1.7	~4	Rechargeable; high energy density; low cost	Fast capacity decay; Short cycle life;

A rechargeable Magnesium-ion battery will be developed and demonstrated by the end of 2012, capable of 400 Wh/kg specific energy and 600 Wh/l energy density in single cells at C/3 discharge rates, with enhanced safety features, faster charging and discharging, and a cycle life of 1000 cycles at 80% depth of discharge.

